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The Synthesis and Characterization of a New Ladder-Type Structure of Compound $[FeMoO_4(phen)]_n$ (phen = 1,10-phenanthroline)

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The drastic expansion of supramolecular chemistry into the solid state reflects the intense contemporary interest in the rational design of functional materials [1–8]. Crystal engineering based on the oxo-bridging of metal ions has resulted in considerable interesting polyoxometalate architectures. The Mo-O-M hetero-metal oxide-based solids (M = Zn(II), Cd(II), Cu(II), Cu(I), and Ag(I) are prototypical of this class such as $[Ni(2,2'\text{-bpy})_2Mo_4O_{13}]$, $[Cu(2,2'\text{-bpy})Mo_2O_7]$, $[Co(2,2'\text{-bpy})Mo_3O_{10}]$ [9], $\{[Cu_3(4,7\text{-phen})_3\}_2\{Mo_{14}O_{45}\}$ [10], $[Cu(phen)MoO_4]$, $MoO_4[FeCl_2(2,2'\text{-bpy})]$, $Mo_3O_{12}\{Fe(2,2'\text{-bpy})\}_2]\cdot 0.25H_2O$ [5] and $[Mo_4O_{15}\{Fe(2,2'\text{-bpy})\}_2]$ [11]. However, the description of structures that contain infinite Mo-O-Fe polymeric motifs has to date been limited. We report here a hydrothermal synthesis and characterization of a new compound $[FeMoO_4(phen)]_n$, which contains a ladder-type Mo-O-Fe motif in the structure.

By hydrothermal method, we prepared the title compound with a mixture of $Na_2MoO_4\cdot 2H_2O$, (2.38 g); $C_{12}N_2H_8\cdot H_2O$, (1,10-phenanthroline, 0.12 g); $FeCl_3\cdot 6H_2O$, (1.82 g); $Na_3C_6H_5O_5\cdot 2H_2O$, (tri-sodium citrate, 2.80 g) and H_2O (15 ml) in a 30 cm^{-1} Teflon lined reactor. The solution was adjusted with NaOH to pH = 10, and heated to 160°C for 72 h. Red crystals were obtained. The yielding crystal material based on Fe is 38%. Calc.: C 36.30, H 2.29, N 7.06, Fe 14.07, Mo 24.17. Found: C 36.21, H 2.26, N 7.01, Fe 14.00, Mo 24.12 (%). *IR* (KBr pellet, cm^{-1}) spectra: ν = 1620s, 1583m, 1560m 1508s, 1490m, 1450m 1420s 1409m, 1335m, 1220m, 1150s, 930s, 875s 842s, 790s, 760m, 720s, 640s,425s, 360s 320m, 390s.

Crystal data were collected on a Siemens P4 four-circle diffractometer with Mo-K_α radiation (λ = 0.70173 Å) and ω-2θ scans. An empirical absorption correction based on ψ-scans was applied. The structure was solved by direct methods and re-

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fined using SHELXL93 software. Pertinent experimental details for the structure determinations are presented in Table 1.

Table 1. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{12}H_8FeMoN_2O_4$
Formula weight	395.99
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1$
a(Å)	8.8815(11)
b(Å)	6.5707(5)
c(Å)	10.630(2)
β(°)	100.40(2)
V(Å^3)	610.14(13)
Z	2
D_{calc}(g cm^{-3})	2.155
μ(mm^{-1})	2.230
F(000)	388
Crystal size(mm)	0.32 × 0.42 × 0.46
Scan mode	ω-2θ
θ(°)	1.95 to 22.49
h	$-1 \to 9$
k	$-1 \to 7$
l	$-11 \to 11$
Reflections collected	1271
Absorption correction	semi-empirical from ψ-scans
Independent reflections	1043
R(int)	0.0155
data/restrains/parameters	1043/73/181
Goodness-of-fit on F^2	1.073
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0217, 0.0558
Final R_1, wR_2 (all data)	0.0230, 0.0568
Largest diff. peak and hole (e.Å^{-3})	0.314, –0.277

$R_1 = \Sigma||F_o| - |F_c||/|F_o|$, $wR_2 = \Sigma w|(|F_o| - |F_c|)^2|/\Sigma[w|F_o|^2]^{1/2}$.

Figure 1 shows a thermal displacement ellipsoid plot (50% probability level) of compound **1**, and depicts the stereochemistry and atom-numbering scheme. The selected bond distances and angles are given in Table 2. The assignment of oxidation state for Mo(VI) atoms and Fe(II) atoms is consistent with the *XPS* spectra (Fe $2p_{3/2}$ 709.85; Mo: $3d_{5/2}$ 232.0 eV). The bond valence calculations made by using the empirical parameters that are given by Brown and O'Keeffe [12] also show that Mo is +6.07. The Fe(II) might come from the reduction of Fe(III) by citrate.

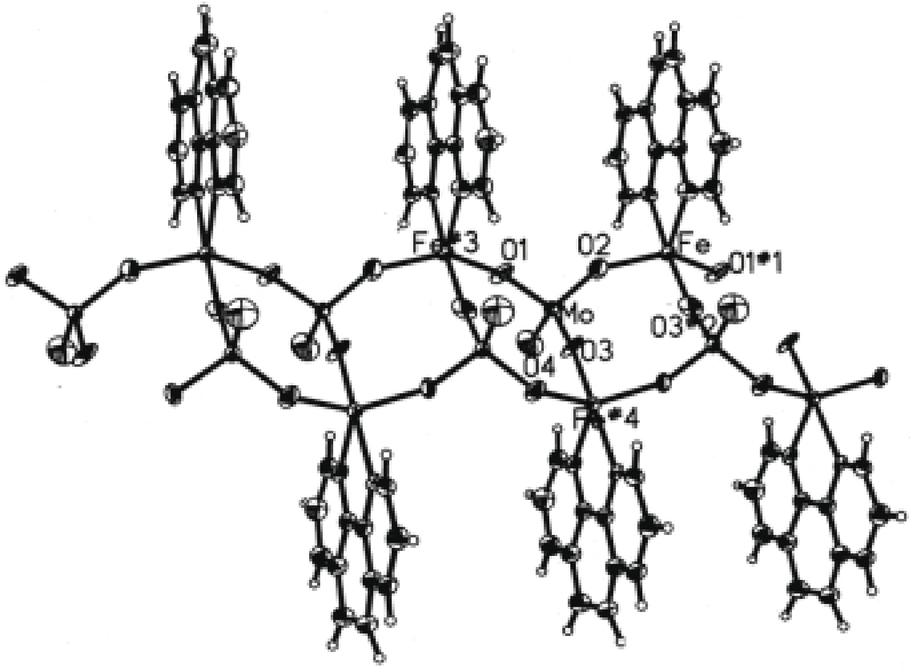

Figure 1. A view of the molecular structure of compound $[FeMoO_4(phen)]_n$.

Table 2. Selected bonds (Å) and angles (°) of compound **1**.

Mo–O4	1.708(4)
Fe–O1#1	1.960(12)
Fe–N2	2.192(4)
Mo–O3	1.747(3)
Fe–O2	2.008(13)
O1–Fe#3	1.960(12)
Mo–O1	1.765(12)
Fe–O3#2	2.071(4)
O3–Fe#4	2.071(3)
Mo–O2	1.794(11)
Fe–N1	2.140(4)
O4–Mo–O3	108.4(2)
O1#1–Fe–O3#2	88.8(6)
O3#2-Fe-N2	174.6(3)
O4–Mo–O1	106.2(10)
O2–Fe–O3#2	93.4(6)
N1–Fe–N2	76.9(2)
O3–Mo–O1	108.7(7)

Table 2 (continuation)

O1#1–Fe–N1	113.0(7)
Mo–O1–Fe#3	158.0(5)
O4–Mo–O2	112.1(9)
O2–Fe–N1	110.1(7)
Mo–O2–Fe	148.9(5)
O3–Mo–O2	112.2(7)
O3#2–Fe–N1	98.0(2)
Mo–O3–Fe#4	170.0(3)
O1–Mo–O2	108.9(2)
O1#1-Fe–N2	91.5(6)
Mo–O4–Fe	114.6(8)
O1#1–Fe–O2	136.1(2)
O2–Fe–N2	90.2(6)

Symmetry transformations used to generate equivalent atoms #1 x, y + 1, z; #2 –x + 1, y + 1/2, –z + 2; #3 x, y–1, z; #4 –x + 1, y – 1/2, –z + 2.

In Fig. 1 there are two kinds of polyhedron units contained in the structure, FeO_3N_2 square pyramid and MoO_4 tetrahedron. The organic *phen* ligands all coordinate to the Fe(II) atoms. By sharing the bridging oxygen atoms, the [FeO_3(phen)] and [MoO_4] groups are linked into zigzag polymeric chains. And, also by sharing bridging oxygen atoms, two zigzag chains are further linked together into a pleated ladder-type structure. The *phen* rings in the structure are all parallel. On a similar zigzag chain, the *phen* rings are arranged on one side of the ladder face. But on the same ladder, the two lines of *phen* rings are anti-formly located on the different side of the ladder face. On the same zigzag polymeric chain, the distance between two neighbour phen rings is 6.60 Å. The oxygen atoms in the structure are divided into two types, the terminal O atoms (of the MoO_4) and the μ_2-bridging O atoms. The μ_2- atoms are used for both propagating of the 1-dimensional zigzag chains (such as O_1 and O_2) and bridging of two zigzag chains together (such as O_3).

Crystal analysis also reveals that in this structure, the hydrogen atoms from *phen* rings on the one 1-dimensional ladder chain, bond to the terminal O atoms from MoO_4 tetrahedron on the neighbour ladder chain into weak (C–H...O) hydrogen bond (C...O = 3.124Å, H...O = 2.390Å, ∠C–H...O = 135.7°). The interconnection of neighbour ladder chains with such type of weak hydrogen bonds results in a 3-dimensional supramolecular framework in the structure.

Finally, the emergence of rare penta-coordinated Fe(II) should be discussed. We know that in an aqueous solution, octa-coordinated Fe(II) ions routinely exist. However, in this structure the penta-coordinated Fe(II) is obviously the most appropriate for Mo and Fe atoms to be bonded into a continuous ladder motif. Due to structural versatility of polyoxometalates, this compound may provide knowledge of transition metal ions, and facilitates the design of more perspective solids.

Crystallographic data for the structure of compound [$FeMoO_4$(phen)]$_n$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC-147741.

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